III.A.21 Dense Membranes for Anode Supported All-Perovskite IT-SOFCs

Objectives

- Synthesize fine, homogeneous, phase pure perovskites in the form of bulk (powders) and thin films to be used as components for developing zero-emission SOFCs capable of operating at reduced temperatures (≈800°C).
- Study of the effect of composition on the microstructure (grain size, grain boundaries, surface texture), magnitude of oxygen permeation, O_2 exchange rates and long term stability.
- Measure the impedance at higher temperatures and investigate the effect of electrical conductivity on the electronic structure using x-ray absorption near edge spectroscopy (XANES) and extended absorption fine structure spectroscopy (EXAFS).
- Assemble an all-perovskite-based SOFC made from a dense ceramic electrolyte membranes ($La_{0.8}Sr_{0.2}Ga_{0.875}Mg_{0.125}O_{3-x}$) sandwiched between porous electrodes (based on Ni as anode and electronically conducting $LaNi_{0.6}Fe_{0.4}O_3$ and/or $La_{0.8}Sr_{0.23}CoO_3$ ceramic cathode).
- Evaluate cost, performance, power generation capabilities, and emissions, while optimizing the reduced dimensionality structures needed to demonstrate a zero-emission demonstrator unit by the end of the three-year period.
- Create interest among undergraduate and graduate African American students to develop theses related to the development of all-perovskite-based anode-supported intermediate temperature solid oxide fuel cells (IT-SOFCs).

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Approach

To make solid oxide fuel cells (SOFCs) commercially viable for environment-friendly energy generation, it is of considerable interest to develop new synthetic techniques for large-scale, cost-effective preparation of perovskite-based multicomponent materials for applications as cathodes, anodes and electrolyte. We are developing inexpensive oxygen-permeable, dense and high surface area membranes in the form of bulk and highly oriented thin films using soft solution chemical routes and pulsed laser deposition techniques for fabricating natural gas fueled, anode-supported all-perovskite planar intermediate temperature SOFCs. Figure 1 shows the schematic of an all-perovskite anode-supported planar SOFC system, under progress at the Solid State Ionics Laboratory of Southern University.

We are investigating the influence of preparation techniques on the microstructure, grain-size and consequently on the electrical transport properties of the ABO_3 structured materials used as electrodes and electrolytes in all-perovskite IT-SOFCs. Wet chemical methods like metal-carboxylate gel decomposition, hydroxide co-precipitation, sonochemical and the regenerative sol-gel process followed by microwave sintering of the powders, have been used. Microwave sintering parameters were optimized by varying sintering time, and temperature to achieve higher density of pellets. Nano-crystalline perovskites with multi-element substitutions at A- and B-sites achieve physico-chemical compatibility for fabricating zero-emission all-perovskite IT-SOFCs.

During this year 2005-2006, we have been investigating the following systems:

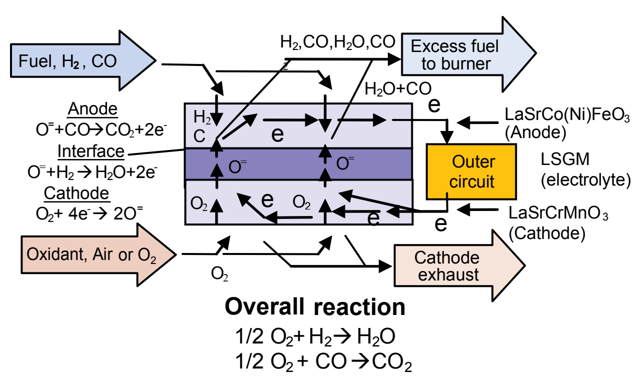

FIGURE 1. All-Perovskite SOFC

1. Hydroxy apatites. $Ca_{10}(PO_4)_6(OH)_2$, stoichiometry and off-stoichiometry compositions prepared by (i) urea combustion, (ii) ball-milling, (iii) hydrothermal, and (iv) Sonochemical reaction. Mg and Sr substitution at the Ca site has also been carried out. Structural and phase behavior investigations are in progress.
2. $Gd_{1-x}Ca_xCoO_3$ systems as novel electrodes for SOFCs and optimization of substitution to find its phase stability and solid solubility of aliovalent and isovalent ions in these matrixes. The glycine nitrate method is used to prepare these compositions.
3. $LaCr_{1-x}M_xO_3$, M = Mn, Mg, Co, Fe, x = 0.1 as interconnect materials and catalytic applications. Phase stability and structural transformation due to substitution on the Cr site. The glycine nitrate method is used to prepare these materials.
4. $LaNi_{1-x}Fe_xO_3$, x = 0.1 –0.9, cathode materials and sensor applications. The glycine nitrate method is used to prepare these materials.
5. $SrCe_{1-x}M_xO_3$ M = Dy, Er, Eu, Tb, x = 0.1 as proton conducting perovskites and its phase stability with respect to the rare earth substitution.

Results

To date, the following electrocerceramic materials were prepared in the form of bulk and thin films using innovative wet chemical processing methods and pulsed laser deposition techniques: 1) nanocrystalline $(La,Sr)(Ga,Mg)O_3$ (LSGM) electrolyte, 2) $La_{0.9}Sr_{0.1}Co_{0.9}M_{0.1}O_3$ (M = Fe, Ni, Mn) cathode, 3) Ni-based perovskite cermet or $(La,Sr)(Ga,Mn)O_3$ (LSGMn) anode, 4) $LaCrO_3$ interconnect, and 5) ceria-based anodic catalyst materials. The exceptional structural and chemical compatibility of LSGM with $La_{0.9}Sr_{0.1}Co_{0.9}M_{0.1}O_3$ (M = Fe, Ni, Mn) as a perovskite-based cathode, and anode, makes it a unique electrolyte for all-perovskite-based IT-SOFCs. To produce submicron LSGM powders for high-quality membrane fabrication, the combustion technique via aqueous solutions is usually preferred to the conventional solid-state mixed-oxide method. The solution route provides many advantages, for example, molecular homogeneous precursors, reduced sintering temperature for obtaining dense ceramics, and controllability of uniform superfine grain size. One major disadvantage of LSGM is the high cost of the gallium containing precursors. Once LSGM materials are used as electrolytes commercially, regeneration of LSGM will be a cost-effective effort. Based on this concern, we have explored the possibility of regenerating the LSGM ceramics to be aqueous solution precursor. Although the solid Ga_2O_3 remains insoluble, our experiments have shown the LSGM ceramics are completely soluble in an acidic solution. In addition, the regenerative route is also cost-effective and time-saving for in-lab researchers who usually prepare large amounts of LSGM samples, for example, to tailor effects of composition or synthesis conditions on the properties of LSGM.

The sintering behavior of the materials prepared from the various routes was examined by scanning electron microscopy (SEM) shown in Figure 2. The pellets prepared by the regenerative sol-gel technique produces nano-crystalline powders which have better sintering properties as indicated in Figure 2a-b and Figure 2c-d.

Recently, the synthesis of and electrical property measurements on nano-crystalline ceria and Gd-doped ceria have been done in our lab. The X-ray diffraction (XRD) and transmission electron microscopy (TEM) results are given in Figure 3 (top and bottom), respectively.

Simultaneously, we have also investigated dense proton conducting (PC) perovskite membranes such as $SrCeO_3$, and $SrCe_{1-x}M_xO_3$ that were synthesized by sonochemical treatment followed by the hydrothermal method and sintering done by microwave heating. Figure 4 shows the electrical conductivity measurements of $SrCeO_3$.

Also, an investigative study was performed for developing materials to fabricate a natural gas fueled SOFC hybridized to a gas turbine (SOFC-GT) to enhance power production and maximum utilization of resources in Trinidad.

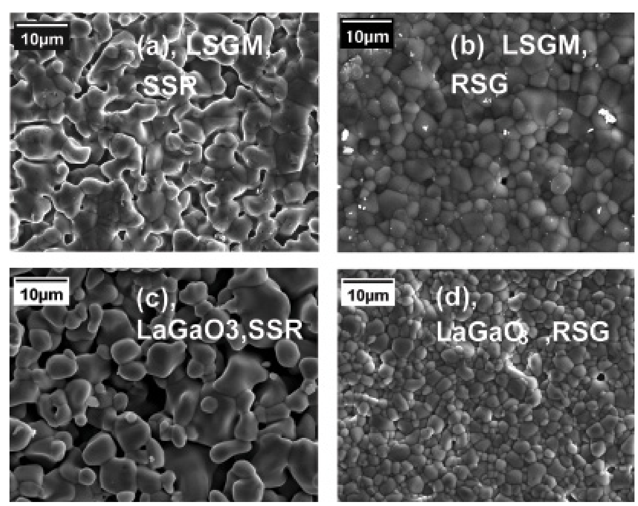

FIGURE 2. SEM Micrographs of $La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{2.825}$ (LSGM-2015) and $LaGaO_3$ Heated at 1,400°C/8h; (a) Solid-State Route (SSR) Pellet of LSGM-2015; (b) RSG Pellet of LSGM-2015; (c) SSR Pellet of $LaGaO_3$; and (d) RSG Pellet of $LaGaO_3$

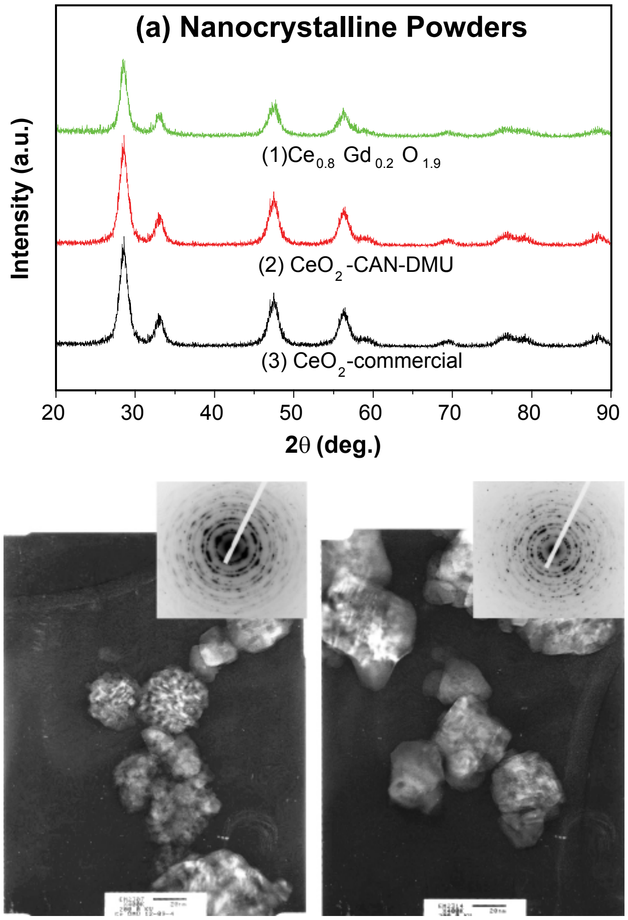

FIGURE 3. XRD Measurements (top) and TEM Photographs (bottom) of Nano-Crystalline Ceria and Gd-doped Ceria

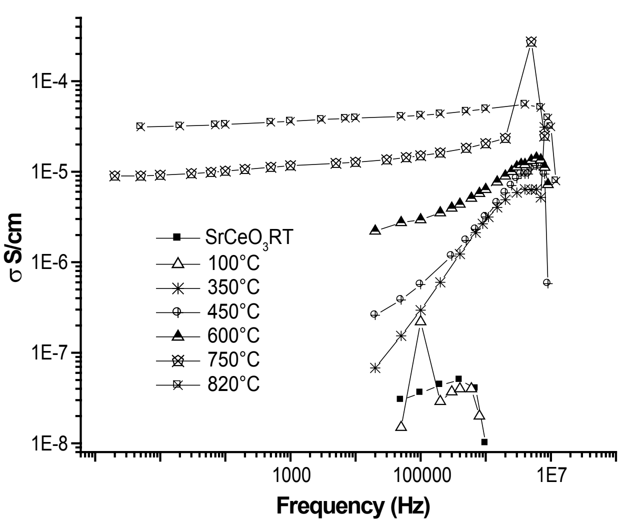

FIGURE 4. Electrical Conductivity Measurements of $SrCeO_3$

FY 2006 Publications

1. Novel wet-chemical synthesis and characterization of nanocrystalline CeO_2 and $Ce_{0.8}Gd_{0.2}O_{1.9}$ as solid electrolyte for intermediate temperature solid oxide fuel cell (IT-SOFC) applications, B.Rambabu, Samrat Ghosh and Hrudananda Jena, J. Mater. Sci. (in press, 2006).

2. An exploratory study on solution assisted synthetic routes to prepare nano-crystalline $La_{1-x}MxGa_{1-y}NyO_3$ (M=Sr, N=Mn,Mg) for IT-SOFC applications. Hrudananda Jena and B. Rambabu, Mater. Chem. Phys. (in Press, 2006).

3. Innovative processing of dense LSGM electrolytes for IT-SOFC's, B. Rambabu, Samrat Ghosh, Weichang Zhao and Hrudananda Jena, J. Power Sources (Accepted), 2006.

4. Effect of sonochemical, regenerative sol gel, and microwave assisted synthesis techniques on the formation of dense electrolytes and porous electrodes for all perovskite IT-SOFCs, Hrudananda Jena, and B. Rambabu, Journal of Fuel Cell Science and Technology, 2006.

5. Proton Transport in Nanocrystalline Hydroxy apatite $(Ca_{10}(PO_4)_6(OH)_2$, Hrudenanada Jena, and B. Rambabu, Accepted for publication in the Journal of Materials Science, (in press 2006).